L.M. Ushakova[1,2], K.O. Ivanenko[1,3], N.V. Sigareva[2], M. I. Terets[2], M.T. Kartel[1,2], Yu.I. Sementsov[1,2]

Influence of nanofiller on the structure and properties of macromolecular compounds

[1]*Ningbo University of Technology No 55-155 Cui Bai Road, Ningbo, China, milushakova@gmail.com*
[2]*Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine 17 General Naumov Str., Kyiv, Ukraine*
[3]*Institute of Macromolecular Chemistry of NAS of Ukraine, 48 Kharkiv highway, Kyiv, Ukraine*

Experimentally, by methods of X-ray phase analysis, temperature-programmable desorption mass spectrometry, electrical resistance, tension and compression, it was found that nanoscale fillers (carbon nanotubes, pyrogenic oxides of silicon, titanium and titanium-silicon, and polymers with structure, mechanical (stress and strain deformation) and thermodynamic (melting and thermodestruction temperatures) properties. According to the results of quantum chemical calculations, such effects can be explained by the interaction of the polymer with the nanofiller and the formation of intermolecular complexes due to intermolecular dispersion forces.

Keywords: carbon nanotubes, pyrogenic oxides, synthetic polymers, biopolymers.

Introduction

The properties of materials are determined by the nature of interatomic interaction, the peculiarities of the structure and its changes under the influence of various factors. The transition to nanometer systems, when the number of atoms (or molecules) of the surface becomes comparable to their number in volume, increases the interaction energy due to "surface tension" (surface energy) without significant changes in structure, and the properties of the whole nanosystems are actually determined by its surface characteristics. When introducing a nanosystem (highly dispersed (pyrogenic) silica (HDS), carbon nanotubes (CNT), graphene nanoparticles (GNP), etc.) into the matrix (polymer, carbon, ceramic) and reaching the flow threshold, ie in the formation of a continuous volume matrix, the nanosystem forms nanoscale regions of the matrix itself and, obviously, causes changes in its structure and properties.

The series of works [1–6] is devoted to the study of the effect of low nanofiller concentrations on the structure, mechanical and electrophysical characteristics of polymer systems based on polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyamide 6 (PA 6) filled with HDS and CNT. Tests for tension and compression of composites PE CNT, PP CNT, PTFE CNT and PTFE HDS showed that the introduction of nanofiller changes the mechanical properties of the composite systems: increases stress and reduces fracture deformation, and in some cases, as for PA 6-CNT - increases both stress and deformation of destruction, ie increases the energy of destruction [6]. Note that for these systems also increases the melting point and thermal destruction, for example, for the PE-CNT system - by almost 60 ° C [5]. In addition, the dependences of both mechanical (Fig. 1 a, b; 2 a, b) and thermodynamic characteristics on the filler content are not monotonic [1–6].

Theoretical analysis performed on different models [7–10] shows that such a change in properties is due to the characteristics of different phases formed at the interface due to the interaction of filler nanoparticles with the polymer chain. Molecular dynamics modeling [7] demonstrates the formation of an ordered layer of polymer matrix around the nanoparticle. This layer, known as interfacial, plays a central role in the overall mechanical response of the composite.
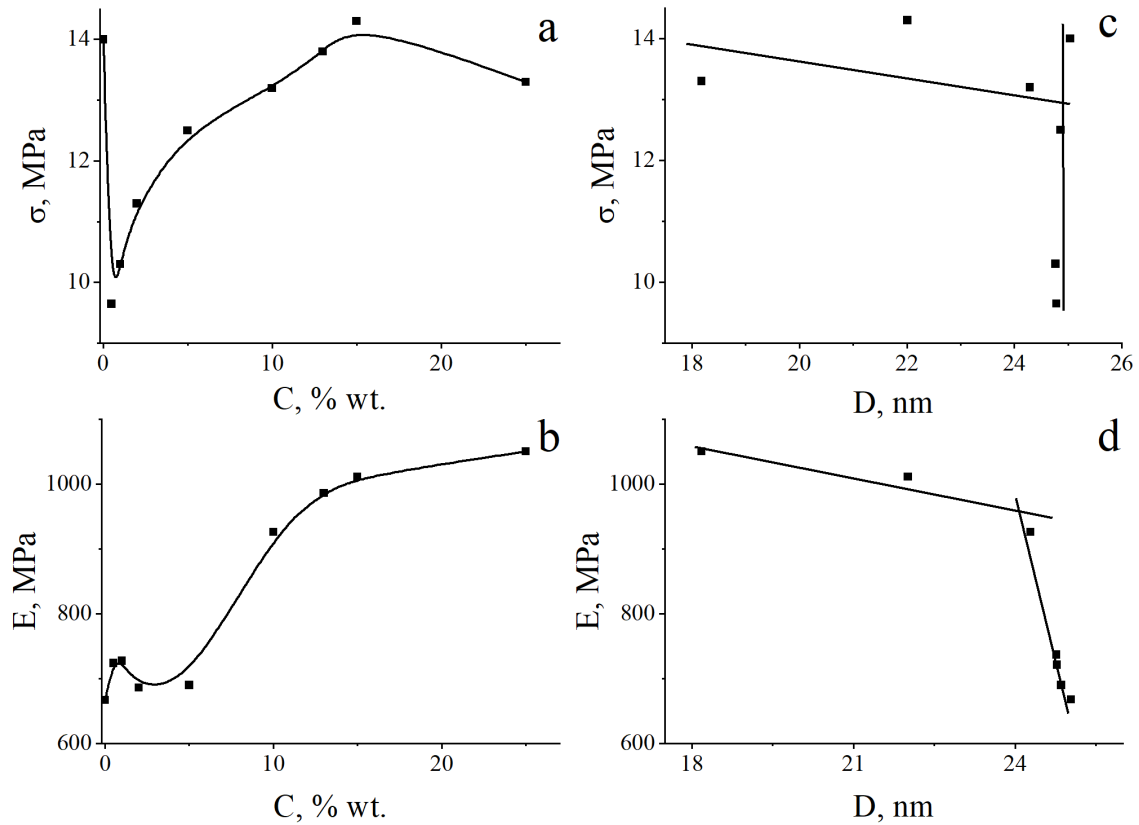
Fig. 1. Dependencies of the conditional yield strength of PTFE–A-300 composites (a, c) and the modulus of elasticity (b, d) on the concentration of CNTs (a, b) and the coherently scattering domains size (c, d).
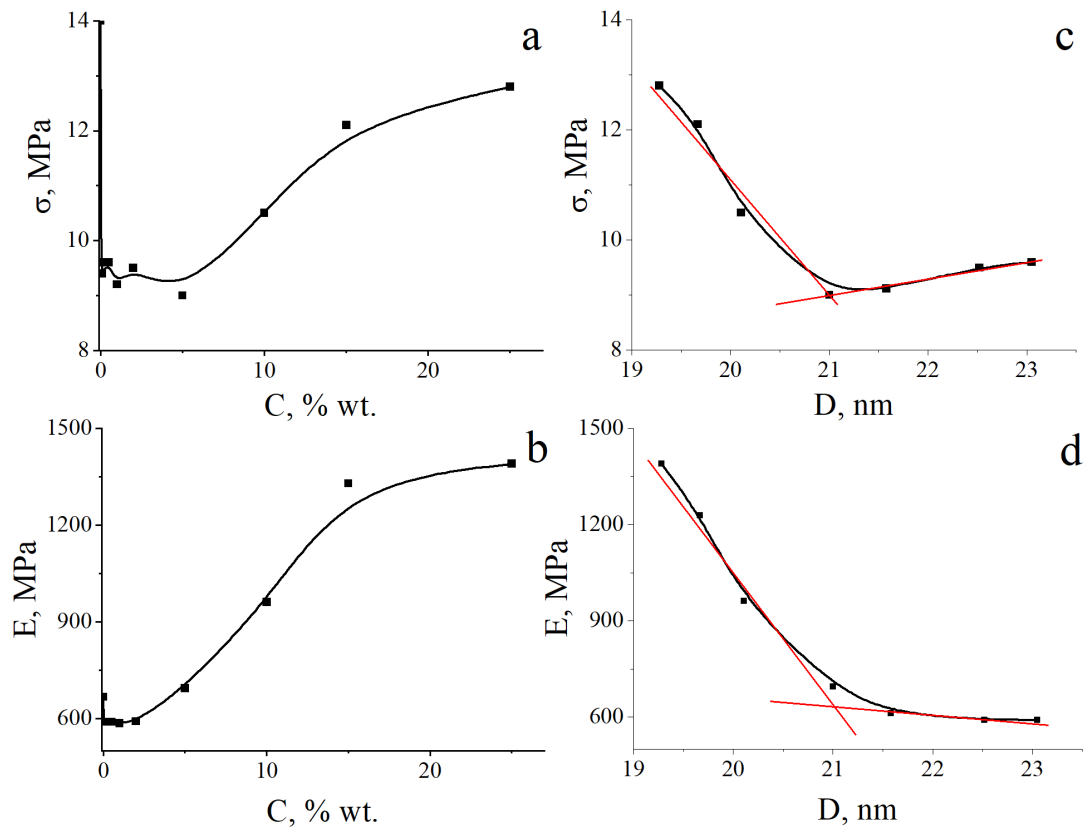

Fig. 2. Dependencies of the conditional yield strength of PTFE–MWCNTs composites (a, c) and the modulus of elasticity (b, d) on the concentration of CNTs (a, b) and the coherently scattering domains size (c, d).

L.M. Ushakova, K.O. Ivanenko, N.V. Sigareva, M. I. Terets, M.T. Kartel, Yu.I. Sementsov

Therefore, the presence of the interfacial surface is considered as the only reason for the strengthening of the characteristics of the composite (mechanical, thermodynamic). If this approach is correct, it is possible to determine with experiments some structural parameter of the system, which would characterize the interfacial surface and show a monotonic change in the strength characteristics of the composite from this parameter. For polymeric materials, the parameter that reflects the effect of the nanofiller on the structural hierarchy of the matrix may be, for example, the size of the coherently scattering domain size (CSD) of the X-ray radiation or the degree of crystallinity [6, 7, 10]. The average size of crystallites is calculated by Scherer's formula [11]. Fig. 1 c,d and 2 c,d show the dependences of the conditional yield strength and modulus of elasticity depending on the value of BCD for the system of PTFE HDS and PTFE CNT, respectively. Similar results were obtained for PE-CNT and PP CNT systems [1].

Thus, the analysis of the dependences of strength on the size of CSD and the content of nanoscale filler revealed that the strength characteristics of the size of CSD are linear and divided into two areas with the boundary of flow threshold between, obviulsy. For example, for the PE CNT system, the size of the CSD D ~ 21 nm. It corresponds to the content of CNT ~ 0.5% vol. and agrees well with the flow threshold defined from the dependence of electrical conductivity on the content of CNTs [1, 5]. Similar results are observed for PP CNT, PTFE CNT and PTFE HDS systems. For the PP CNT system, the size of the CSD is approximately 11.2 nm, PTFE CNT - ~ 21 nm, and for PTFE HDS - ~ 24 nm [1].

The quantum chemical calculation of the interaction values of CNT fragments with polyethylene and polypropylene oligomers carried out in [12] showed that the interaction energy of the carbon nanotube fragment with the polypropylene oligomer is larger than that of polyethylene. It can explain the smaller size of coherent scattering for the PP-CNT system. Since the polymer with the outer surface of the carbon nanotube forms an intermolecular complex that is not covalently bound and held by intermolecular dispersion forces [12], ie oligomers of polymers and nanotube surfaces in the formed nanocomposites are closer than each other.

Epoxy, urea-formaldehyde, polyester resins are widely used as binders for the production of fiberglass and carbon fiber, and other composite materials based on fabric. Such materials are used in aerospace, automotive and shipbuilding. The studies of thermal destruction of polymer nanocomposites based on polyester, epoxy and urea-formaldehyde resins filled with HDS, undertaken in works [13–17] are important not only for understanding the mechanisms of changes in the rate of physicochemical reactions during material formation, strength characteristics of composites, but are also important for industrial production.

The creation of nanocomposites based on disaccharide-modified (lactose and sucrose) HDS surface is important for the adsorption of N-acetylneuraminic acid to regulate the physiological state of cells used in biotechnology and is an urgent and important problem today both scientifically and practically [18, 19].

The purpose of this work is to expand the class of studied polymers, namely, to study the structure and properties of some synthetic and biopolymers filled with nanoscale pyrogenic oxides.

I. Materials and methods of research

Urea-formaldehyde resins (URF) brand КФБ-1 (Ukraine), filled HDS brand A-300 with a specific surface area - S_f ~280 m^2/g, effective diameter $2R_f$ ~ 5 – 20 nm, titanium dioxide particles TiO_2 ($S_f \approx 10$ m^2/g, $2R_f \approx 31$ нмнм) and titanium silicon SiO_2/TiO_2 ($S_f \approx 48$ m^2/g $2R_f \approx 42$ nm,) (ST-40) for content 1,5 mass %.

Nanoscale oxides were introduced into the URF using a mechanical stirrer at constant speed. To evenly distribute and avoid agglomeration of the filler, the composite was dispersed (УЗДН-А).

To create HDS-disaccharide nanocomposites the following components were used: A 300 pyrogenic silica, sucrose (α-D-glucopyranosyl-β-D-fructo-pyranoside, "Reachim"), lactose (β-galactopyranosyl 1 → 4-α-gluco -pyranosis, "Sigma");

Modification of the HDS surface was carried out by adsorption of saccharides from the liquid phase at a temperature of $20 \pm 3°C$ (single solutions in concentrations - 10^{-2}-10^{-3} mol/l, portions of calcined silica - 100 mg, adsorption time - 2 h).

Equipment for temperature-programmable desorption mass spectrometry includes a monopoly mass analyzer MX-7304A (Selmi, Sumy, Ukraine). The test samples are placed into the vacuum molybdenum quartz tube (under the pressure of 10^{-1} Pa) with programmable temperature change in the range of 25–800°C. Accuracy of temperature measurement: ± 0,05°C. The rate of temperature change does not exceed 8°C/min. From the tube volatile products of thermal decomposition of the samples through a high-vacuum valve and a quartz tube length of 20 cm, heated to a temperature of at least 150°C, enter the input system of the mass analyzer. Decomposition products enter the ionization chamber of the mass spectrometer through a high-vacuum valve, get ionized and fragmented by electrons. Registration and analysis of mass spectra of decay products of the sample is performed by an automated system of registration and data processing based on a personal computer.

II. Research and discussion results

TPD mass spectrometry of URF nanoxide systems. The mass spectrum of unfilled URF is characterized by three m/z intervals of registered decay products (Fig. 3). In the first interval 15≤m/z <20 the main peaks belong to the hydroxyl group OH (m/z 17), water molecules (m/z 18) and H_2OH (m/z 19). The highest intensity of mass spectral lines in the temperature range of 30 <T <180°C is observed for ions with m/z ≤ 50, at 180 <T <202°C the appearance of ions with m/z 58 – 77 and m/z 81 at ≈ 245 °C. The main intense lines in the mass spectrum of thermal destruction of URF belong to ions with m/z 18 (H_2O), 27 (HCN), 28 (CO), 43 (CH_2-NH),
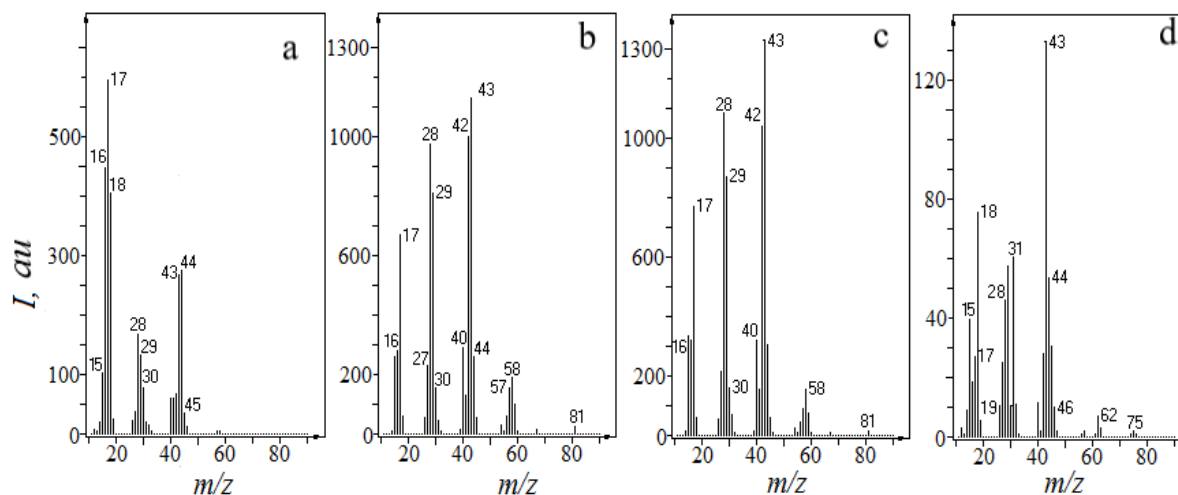
Fig. 3. Mass spectra of thermodestruction: initial URF (a); of URF-nanooxide composites: HDS (b), titanium dioxide (c), titanium-siica (d) (T ~ 230 ° C)

57 ($CH_2 = CH-NHCH_3$), 58 ($NOCNH_2$) in the temperature range 25 <T <800°C (Fig. 3).

The initial stage of thermal destruction of the polymer macromolecule occurs due to the presence of water molecules on the surface of the filler, in the condensed or physically bound state. It is known that carbonyl (=C=O), amino (-NH-), and hydroxyl groups (-OH) in thermosetting URF form coordination bonds by donor-acceptor mechanism [20, 21]. Decomposition products with m/z ≥ 27 are structural elements of polymer chains (depicted in the structural formula of the elementary unit of URF) [17]:

Fig. 4 shows the thermodesorption curves of water (m/z 18) at a temperature of 10 – 800°C. Desorption of water in the range of 62 – 277°C is characterized by two temperature maxima of spectra at T_{m1} = 171 ℃ and T_{m2} = 214℃.

Fig. 5 presents the TPD spectrum for products with m/z 27 (HCN), 30 (OCH_2), 42 (N-CH_2-N), 57 (CH_2 = CH-$NHCH_3$) thermal destruction of URF (1) and resins with HDS (2), titanium dioxide (3) and titanium silica (4).

Fig. 5 shows that the thermograms of the volatile product of destruction from m/z 27 (a) of composites with titanium-silica gets its maximum at T~250°C. When considering the thermal destruction of resin composites with highly dispersed silica and titanium dioxide, it should be noted that in the range of low and high temperatures there is a significant difference in both curve forms and temperature maxima with increasing intensity of volatile degradation products. It follows that the filling of SiO_2 and TiO_2 nanoparticles enhances the thermal destruction of composites.

One of the features of the change in T_m of the decay products of compositions with SiO_2 and TiO_2 is the shift towards lower temperatures by~22 – 44°C (Fig. 5). A band of destruction with Tm~620°C also appears on the thermodesorption curves of the fragments with m/z 27. The appearance of high-temperature degradation bands probably indicates the destruction of the bond of the fixed polymer chains on the active surface centers of SiO_2 and TiO_2 fillers when the temperature reaches – 500°C.

Desorption peaks are shifted to the region of low temperatures, which points to a decrease in heat resistance of composites.

TPD mass spectrometry modified HDS disaccharides. The thermal decomposition of disaccharides (lactose, sucrose) adsorbed on the surface of HDS was studied by the TPD MS method.

Comparative mass spectrometric studies of thermolysis of sucrose in the condensed state and adsorbed on the surface of HDS have shown that the interaction with HDS leads to an increase in the decomposition temperature of these compounds and changes the nature of the process. Thermolysis of sucrose in the condensed state (Fig. 6, a) occurs in one stage in the temperature range of 120-220°C. For sucrose adsorbed on the surface of HDS (Fig. 6, b), the shift of the maximum decomposition towards higher temperatures and the appearance of three stages (172, 276, 410°C) is recorded.

When thermolysis of sucrose is in the condensed state the release of carbon-containing compounds takes place, while for sucrose adsorbed on the surface of HDS (Fig. 5, b), thermolysis of the sample is accompanied by its dehydration (17 Da) and the release of CO molecules with mass m/z = 28 Da and molecules CO_2 with mass m/z = 44 Da. This indicates the stabilization of the saccharide molecule on the surface of HDS.

In case of sucrose adsorbed on the surface of silica (Fig. 6, b), the destruction process is proceeding in three stages with maxima at 172, 276 and 410°C, but the intensity of the peaks decreases. As in the condensed state, the process of dehydration of H_2O (m/z 17 Da) takes place, the release of the CO molecule (m/z 28 Da), although there are two lines non-relevant for the thermolysis of sucrose in the condensed state - C_4H_6O with a mass of m/z 70 Da and C_5H_5O with a mass of m/z 81 Da.

Condensation of lactose in the condensed state is proceeding in three stages with cleavage of pyranose cycles of glucose and galactose and dehydration of the sample. For the thermogram of lactose in the adsorbed state, the decomposition maxima have a shift towards lower temperatures and lower intensity (Fig. 7, b)
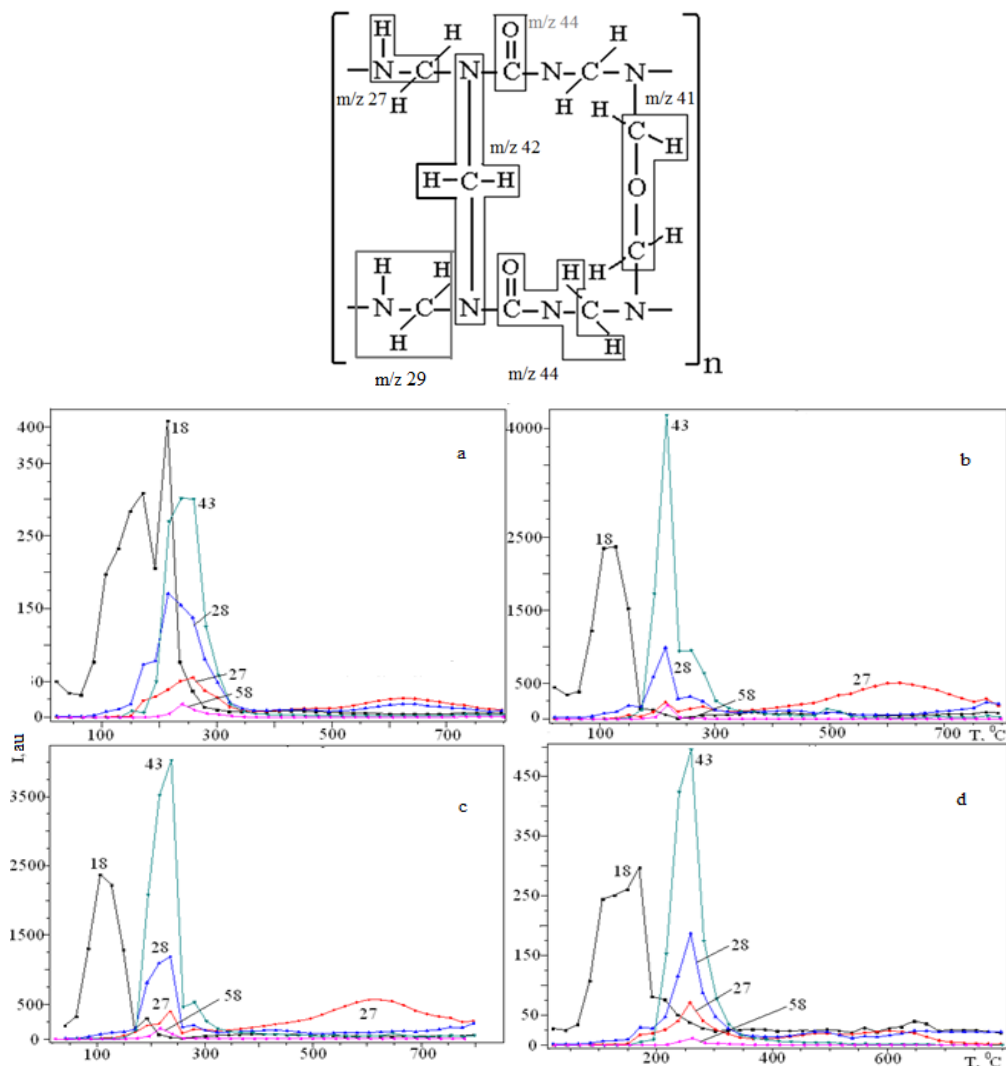
L.M. Ushakova, K.O. Ivanenko, N.V. Sigareva, M. I. Terets, M.T. Kartel, Yu.I. Sementsov

Fig. 4. Degradation thermograms: URF (a), URF filled with HDS (b), titanium dioxide (c), titanium silica for products with m/z 18, 27, 28, 43, 58 (d).
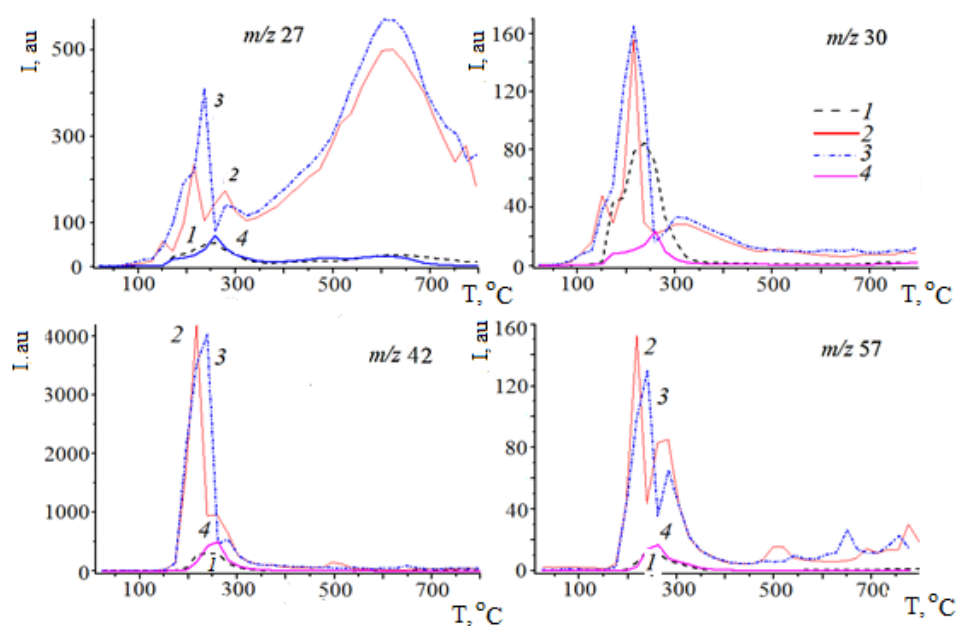

Fig. 5. Decomposition thermograms of URF (1) and resin with 1.5% silicon dioxide (II) (2), titanium dioxide (3) and titanium silicon (4) products with m/z 27 (HCN), 30 (OCH_2), 42 ($N-CH_2-N$), 57 ($CH_2 = CH-NHCH_3$).
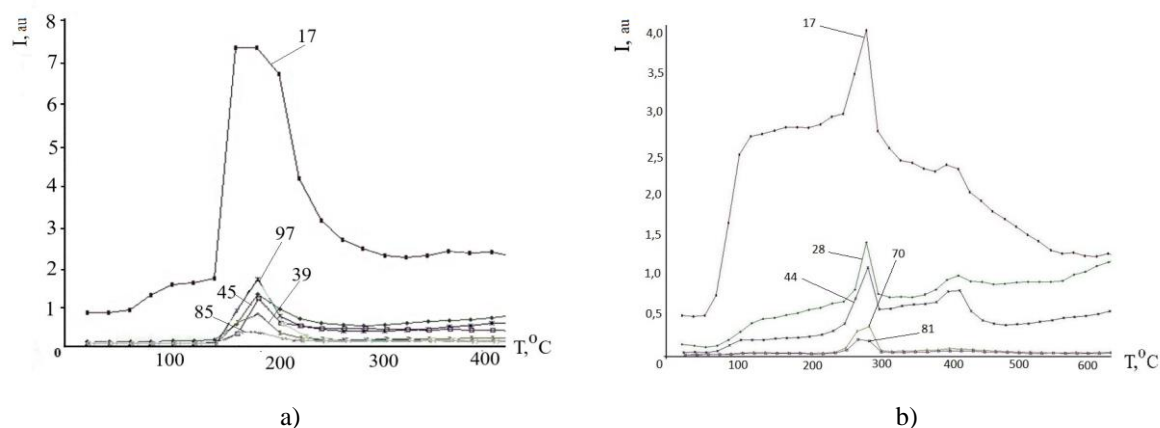
398

Fig. 6. Thermolysis of sucrose in the condensed state (a), thermolysis of sucrose adsorbed on the surface of VDK (b).
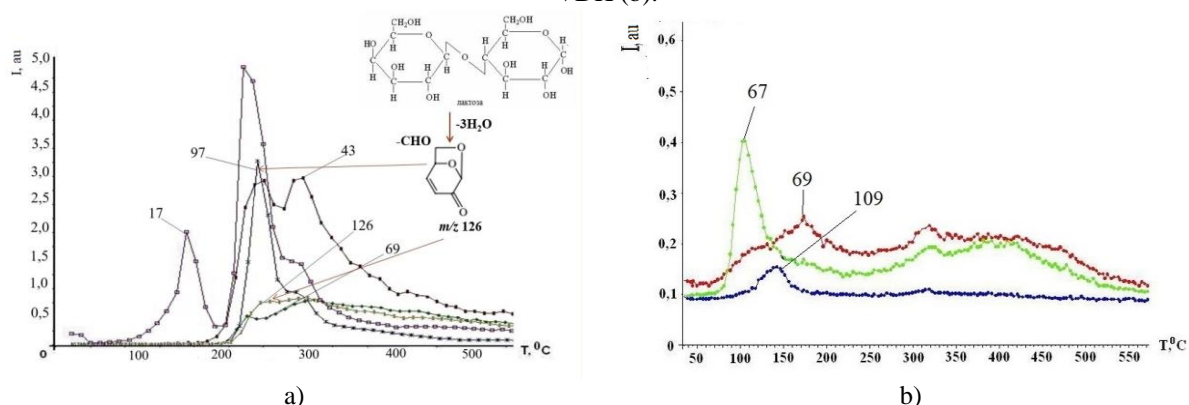

Fig. 7. Thermolysis of lactose in the condensed state (a), thermolysis of lactose in the complex with HDS (b).

Conclusions

The nanofiller enhances the ordering of the polymer matrix. The effect of the polymer structure stabilization for composites with URF with oxide particles is realized with more chemically active filler - titanium-silica. The effect is related to the fixation of unbound fragments of the polymer structure on the active surface centers of the filler particles and the chemical interaction of the atoms of the formed polymer chains with the surface centers.

Comparison of TPD mass spectrometric studies of sucrose and lactose thermolysis in condensed and adsorbed states on the HDS surface shows that the interaction with HDS leads to an increase in the decomposition temperature (destruction) of these compounds and changes the nature (intensity) of the process.

Therefore introduction of low nanofiller content into polymer matrices of different nature changes their structure, mechanical (stress and deformation fracture) and thermodynamic (melting and thermodestruction temperatures) characteristics, which may be due to intermolecular interaction of polymer with nanofiller and intermolecular complex formation.

Ushakova L.M. - PhD in Chemistry*;*
Ivanenko K.O. – PhD in Physics and Mathematics*;*
Sigareva N.V. – PhD in Physics and Mathematics*;*
Terets M.I. – PhD in Chemistry;
Kartel M.T. – Academician NAS of Ukraine, Professor, D-r of Science (Chemistry)*;*
Sementsov Y.I. – D-r of Science (Physics and Mathematics), Senior Researcher.

[1] K.O. Ivanenko, L.M. Ushakova, T.G. Avramenko, S.L. Revo, M.T. Kartel, Yu.I. Sementsov, Springer Proceedings in Physics 246, 685 (2021); https://doi.org/10.1007/978-3-030-51905-6_46.
[2] Yu.I. Sementsov, M.T. Kartel, Himia, Fizika ta Tehnologia Poverhni 10(2), 174 (2019); https://doi.org/10.15407/hftp10.02.174.
[3] Yu. Sementsov, O. Cherniuk, G. Dovbeshko, S. Zhuravskyi, S. Makhno, B. Wang, M. Kartel, Journal of Materials Science and Chemical Engineering 7(7), 26 (2019); https://doi.org/10.4236/msce.2019.77004.
[4] Yu. I. Sementsov, Formation of structure and properties of sp2-carbon nanomaterials and functional composites with their participation (Interservice, Kyiv, 2019), p.198–205.
[5] Yu.I. Sementsov, S.N. Makhno, S.V. Zhuravsky, M.T. Kartel, Himia, Fizika ta Tehnologia Poverhni 8(2), 107 (2017); https://doi.org/10.15407/hftp08.02.107.

[6] M. Kartel, Yu. Sementsov, S. Mahno, V. Trachevskiy, W. Bo, Universal Journal of Materials Science 4(2), 23 (2016); https://doi.org/10.13189/ujms.2016.040202.

[7] M. Malagù, M. Goudarzi, A. Lyulin, E. Benvenuti, A. Simone, Composites Part B 131, 260 (2017); https://doi.org/10.1016/j.compositesb.2017.07.029.

[8] M. Cen-Puc, A. I. Oliva-Avilés, F. Avilés, Physica E : Low-dimensional Systems and Nanostructures 95, 41–50 (2018); https://doi.org/10.1016/j.physe.2017.09.001.

[9] J.C. Halpin, J.L. Kardos, Polym. Eng. Sci 16(5) 344 (1976); https://doi.org/10.1002/pen.760160512.

[10] A. Haque, A. Ramasetty, Composite Structures 71, 68 (2005); https://doi.org/10.1016/j.compstruct.2004.09.029.

[11] A. Patterson, Phys. Rev. 56(10), 978 (1939); https://doi.org/10.1103/PhysRev.56.978.

[12] M.I. Terets, E.M. Demianenko, S.V. Zhuravsky, O.A. Chernyuk, V.S. Kuts, A.G. Grebenyuk, Yu.I. Sementsov, L.M. Kokhtych, M.T. Kartel, Himia, Fizika ta Tehnologia Poverhni 10(1), 75 (2019); https://doi.org/10.15407/hftp10.01.075.

[13] N.V. Poltorayska, B.M. Gorelov, O.O. Tkachenko, Voprosy khimii i khimicheskoi tekhnologii 5, 94 (2012); http://nbuv.gov.ua/UJRN/Vchem_2012_5_21.

[14] N. V. Sigareva, B. M. Gorelov, D. L. Starokadonskyi, Surface 5(20), 204 (2013); http://dspace.nbuv.gov.ua/handle/123456789/149445.

[15] B.M. Gorelov, T.Yu. Gromovoy, N.V. Sigareva, Surface 5(20), 215 (2013); https://doi.org/10.15407/Surface.

[16] B. Gorelov, A. Gorb, O. Korotchenkov, A. Nadtochiy, O. Polovina, N. Sigareva J. Appl. Polym. Sci., 132, 42010 (2015); https://doi.org/10.1002/app.42010.

[17] B.M. Gorelov, V.N. Mistchenko, A.G. Girchenko, Surface 1(16), 136 (2009); https://doi.org/10.15407/Surface.

[18] L.M. Ushakova, B.G. Mischanchuk, N.P. Galagan, V.O.O. Pokrovskij, O.O. Chujko, Biophysical Bulletin 28, 75 (2012); https://periodicals.karazin.ua/biophysvisnyk/article/view/2506.

[19] L.M. Ushakova, Ph.D. dissertation, O. Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine, 2021.

[20] A.A. Tager, Fizikokhimiia polimerov (Khimiia, Moscow, 1978).

[21] S. Xu,·H. Xiao, Y. Chen, J. Li, Ke Jiang, X. He, J. Zhang, Y. Jiang, X. Huang, J. Xie, J. Qi, Journal of Thermal Analysis and Calorimetry 140, 1331 (2020); https://doi.org/10.1007/s10973-020-10079-1.

Л.М. Ушакова[1,2], К.О. Іваненко[1,3], Н.В. Сігарьова[2], М. І. Терець[2], М.Т. Картель[1,2], Ю.І. Семенцов[1,2]

Вплив нанонаповнювача на структуру та властивості високомолекулярних сполук

Технологічний університет Нінбо, № 55-155 Сиі Bai Road, Нінбо, 315016, Китай, milushakova@gmail.com
Інститут хімії поверхні імені О.О. Чуйка НАН України вул. Генерала Наумова, 17, Київ, 03164, Україна
Інститут хімії високомолекулярних речовин НАН України, Харківське шосе, 48, м. Київ, 02160, Україна

Експериментально, методами рентгенофазового аналізу, температурно-програмованої десорбційної мас-спектрометрії, електроопору, розтягу та стискання, встановлено, що нанорозмірні наповнювачі (вуглецеві нанотрубки, пірогенні оксиди кремнію, титану та титанокремнезему) при взаємодії з деякими біо-, сітчастими та лінійними полімерами змінюють їхню структуру, механічні (напругу та деформацію руйнування) і термодинамічні (температури плавлення та термодеструкції) властивості. За результатами квантово-хімічних розрахунків такі ефекти можуть бути пояснені взаємодією полімеру з нанонаповнювачем і утворенням міжмолекулярних комплексів за рахунок міжмолекулярних дисперсійних сил.

Ключові слова: вуглецеві нанотрубки, пірогенні оксиди, синтетичні полімери, біополімери.